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(54) ADHESIVE PELLICLE FILM AND PELLILCLE

(57)Abstract:
PURPOSE: To provide an adhesive pellicle film excellent in adhesiveness and light transmissivity and having excellent light resistance even to light having such short wavelength as 360-450nm.
CONSTITUTION: An adhesive material layer made of fluorine-contg. poly-(meth) acrylate is formed on one side of a transparent thin film of fatty acid ester of cellulose. The poly(meth)acrylate is a copolymer of 20-80mol% monomer (A) represented by a formula CH2=C(R1)-COOR2 (where R1 is H or methyl and R2 is straight chain fluoroalkyl) with 80-20mol% monomer (B) represented by a formula CH2=C(R3)-COOR4 (where R3 is H or methyl and R4 is branched fluoroalkyl) and has 0.10-0.35dl/g intrinsic viscosity (η) measured in m-xylene hexafluoride at 60°C. The objective adhesive pellicle film for exposure with light having such short wavelength as 360-450nm is obtd.

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CLAIMS

[Claim(s)]
[Claim 1] To one field of the fatty-acid-ester transparent thin film of a cellulose, it is a general formula [1].
[Formula 1]

$$CH_2=C(R^1)-COOR^2 \qquad [1]$$

(-- in R1, a hydrogen atom or a methyl group, and R2 show a straight chain-like fluoro alkyl group among a formula At least one sort of monomers (A) expressed with), and general formula [2]
[Formula 2]

$$CH_2=C(R^3)-COOR^4 \qquad [2]$$

(In R3, a hydrogen atom or a methyl group, and R4 show the fluoro alkyl group of the letter of branching among a formula.) The adhesive pellicle film with a wavelength of 360-450nm for short wavelength light exposure with which the constituent rate of the monomer in a copolymer (A) is characterized by forming the slime layer which consists of fluorine-containing poly (meta) acrylate whose limiting viscosity [eta] which the 20 - 80-mol constituent rate of % and a monomer (B) measured in 80 - 20-mol hexa [meta-xylene] FURUORAIDO which is % and is 60 degrees C is 0.10 - 0.35 dl/g.
[Claim 2] The adhesive pellicle film according to claim 1 characterized by the limiting viscosity [eta] of a copolymer being larger than 0.20 dl/g, and being 0.35 or less dl/g.
[Claim 3] The adhesive pellicle film according to claim 1 or 2 characterized by for the constituent rate of the monomer in a copolymer (A) having more more than 20 mol % or less than [45 mol %], and constituent rates of a monomer (B) than 55-mol %, and being less than [80 mol %].
[Claim 4] The adhesive pellicle film according to claim 1 or 2 characterized by for there being more constituent rates of the monomer in a copolymer (A) than 75-mol %, and less than [80 mol %] and the constituent rate of a monomer (B) being more than 20 mol % or less than [25 mol %].
[Claim 5] The pellicle characterized by the bird clapper from an adhesive pellicle film and a pellicle frame according to claim 1 to 4.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] In case this invention manufactures semiconductor devices and liquid crystal display boards, such as LSI and a VLSI, it relates to the pellicle for lithography (henceforth a pellicle) which prevents that dust adheres to the mask used at a lithography process.
[0002]
[Description of the Prior Art] In case a semiconductor device and a liquid crystal display board are manufactured, a mask (exposure negative) is used for irradiating light and making a pattern imprint on a substrate. If dust adheres to this mask, the absorption of light and incurvation by dust take place, the imprinted pattern deforms, or a pattern edge will ill-behaved-result and will carry out, and also a ground will become dirty black and will cause the fall of the size of a product, quality, appearance, etc. Therefore, the imprint work of a pattern is usually done in a pure clean room. However, even if it is in the atmosphere of a clean room, it is difficult to always keep a mask pure in fact. Then, it has prevented dust adhering to a mask by sticking on the front face of the above-mentioned mask the pellicle which has good light-transmission nature. Dust adheres to a pellicle front face and stops namely, adhering to a mask front face directly by use of a pellicle. Therefore, if the focus is doubled on the pattern of a mask at the time of a lithography process, the bad influence to the imprint by dust will not be seen.

[0003] The fundamental composition of the pellicle which plays such a role The black pellicle frame 1 which generally consists of aluminum, stainless steel, polystyrene, etc. as shown in drawing 1 , The transparent pellicle film 2 excellent in the light-transmission nature which was moreover stretched by the end face through the adhesives layer (not shown) and which consists of a nitrocellulose, cellulose acetate, etc., It consists of an adhesive layer 3 prepared in the soffit of the pellicle frame 1 in order to equip a mask, and a mold release layer (separator) 4 for protecting an adhesive layer 3. In order to make the upper-limit side of the pellicle frame 1 stretch the pellicle film 2, there is the method (refer to a U.S. Pat. No. 4861402 specification and JP,63-27,702,B) of pasting up with the adhesives which consist of a method (refer to JP,58-219023,A) of making the pellicle frame 1 applying and air-drying the good solvent of the pellicle film 2, acrylic resin, an epoxy resin, etc. As described above, since a pellicle is used at a lithography process, a high detergency is required of the composition member. Since possibility that especially the medial surface of a pellicle frame will pollute a reticle front face if the foreign matter has adhered becomes large, a high detergency is required. Generally, the medial surface of a pellicle frame is coated with about 10-50 micrometers of adhesive resins so that the foreign matter adhering to the medial surface may not be omitted. Although the adhering foreign matter is held by this, depending on the size of a foreign matter, or the state of adhesion, it may not be held completely. Then, the adhesion dust particle inspection of the pellicle within the limit side is conducted at the time of pellicle manufacture and the receiving inspection before use etc.
[0004]
[Problem(s) to be Solved by the Invention] However, generally, a pellicle frame front face is roughened by sandblasting or chemical polishing, and it changes it into the lusterless state. Therefore, when the pellicle within the limit side was coated with the adhesive resin, since the roughened front face was entered, it comes to have reflected inspection light irregularly and distinction with the reflected light and irregular reflection light by the foreign matter was not attached, it would be visible, or this resin will overlook the foreign matter which should originally be detected, as many foreign matters have adhered to the pellicle within the limit side, as a result had caused the fall of the yield.
[0005] Then, this invention suppresses the scattered reflection of the light by coating the pellicle within the limit side with an adhesive resin, and aims at offering the pellicle which can perform certainly and easily foreign matter detection of the pellicle within the limit side.
[0006]
[Means for Solving the Problem] That the above-mentioned technical problem should be solved, as a result of repeating examination wholeheartedly, by making surface roughness of the pellicle within the limit side into predetermined within the limits, this invention person was the pellicle within the limit side which coated the adhesive resin, finds out that the scattered reflection of inspection light can be suppressed, and came to complete this invention based on this knowledge. That is, this invention is a pellicle for lithography characterized by for the surface roughness of the pellicle within the limit side being in the range of 0.3-0.9 micrometers of Ra, 4.0-8.5 micrometers of Rt(s), and 0.3-1.1 micrometers of RMS, and coating the

pellicle within the limit side with the adhesive resin.
[0007]
[Embodiments of the Invention] Hereafter, this invention is explained in detail with reference to a drawing. As the pellicle of this invention is shown in drawing 1 , the pellicle film 2 is stretched through an adhesives layer (not shown) to the upper-limit side of the pellicle frame 1, it is what coated the medial surface of the pellicle frame 1 with the binder, an adhesive layer 3 is usually further formed in the lower part of the pellicle frame 1, and the mold release layer 4 which can exfoliate is stuck on the soffit side.
[0008] About the quality of the material of the pellicle frame 1, the resins and blue glass which especially limitation does not have, for example, are used conventionally, such as the anodizing object of aluminum material, stainless steel, a polyacetal, a polycarbonate, PMMA, and acrylic resin, are mentioned. Although the front face of the pellicle frame 1 is usually roughened, the method is not limited but the method by sandblasting or chemical polishing is mentioned. For example, when aluminum material is used, a Carborundum, a glass bead, etc. perform blast processing and the method of carrying out chemical polishing and roughening a front face by NaOH etc., further, is learned.
[0009] In order to adhere, and to hold a foreign matter and to prevent generating of dust, pellicle frame 1 medial surface is coated with an adhesive resin. A silicone system binder, an acrylic binder, etc. are illustrated as an adhesive resin. Moreover, it is made for coating to become 10-50 micrometers in thickness.
[0010] When the surface roughness of pellicle frame 1 medial surface is measured with a sensing-pin formula surface roughness plan, it is made to become the range of 0.3-0.9 micrometers of Ra, 4.0-8.5 micrometers of Rt(s), and 0.3-1.1 micrometers of RMS in this invention. Although reflecting inspection light irregularly and taking as a foreign matter will be lost in order that this resin that entered in the irregularity on the front face of a medial surface may bury irregularity if the pellicle within the limit side is coated with an adhesive resin when the surface roughness of pellicle frame 1 medial surface is smaller than the value specified by this invention There is a possibility of mistaking noting that a laser beam reflects on the pellicle within the limit side and a foreign matter exists on a pellicle film when inspecting the foreign matter on the pellicle film 2 with the test equipment of a laser dispersion method since the reflected light in the pellicle within the limit side becomes large for example. On the other hand, if the pellicle within the limit side is coated with an adhesive resin while the amount of the light scattered about on the pellicle within the limit side can be lessened when the surface roughness of pellicle frame 1 medial surface is larger than the value specified by this invention If this resin that entered in the irregularity on the front face of a medial surface reflected inspection light irregularly and many foreign matters have adhered to the medial-surface front face, misconception will arise. When the foreign matter has actually adhered, inspection not only becomes difficult, but it may overlook this, consequently a pellicle is used, this foreign matter will be omitted, it will adhere to a reticle front face, and the fall of the yield will be caused.
[0011] About the quality of the material of the pellicle film 2, there is especially no limitation and the nitrocellulose currently used conventionally, cellulose acetate, a cellulose propionate, amorphous fluorine polymer, etc. are illustrated. As amorphous fluorine polymer, SAITOPPU (the Asahi Glass Co., Ltd. make, tradename) and Teflon AF (the Du Pont make, tradename) are mentioned, for example. You may use these polymer if needed at the time of production of a pellicle film, dissolving in a fluorine system solvent etc.
[0012] Although fluorine system polymer, such as a polyacrylate adhesive, an epoxy resin adhesive, silicon resin adhesive, and fluorine-containing silicone adhesives, is mentioned, fluorine system polymer is [that what is necessary is just to choose suitably what is used conventionally also about the quality of the material of an adhesives layer] especially suitable. As fluorine system polymer, fluorine system polymer CT-69 (the Asahi Glass Co., Ltd. make, tradename) is mentioned. What is necessary is just to form, using a pressure sensitive adhesive doudle coated tape, a silicone resin binder, an acrylic binder, etc. as an adhesive layer 3. What is necessary is just to choose a silicone release agent, a fluorine denaturation silicone release agent, etc. which are generally used also about the quality of the material of the mold release layer 4. moreover, each above-mentioned pellicle composition -- the size of a member of especially limitation is good like [there is nothing and] the usual pellicle then
[0013] What is necessary is to stretch the pellicle film 2 through an adhesives layer by the usual method to the upper-limit side of the pellicle frame 1 which coated the medial surface with the adhesive resin, and to form an adhesive layer 3 in the soffit side of the pellicle frame 1, and just to stick the mold release layer 4 suitably, so that it can exfoliate in the soffit side of this adhesive layer 3 in order to manufacture the pellicle of this invention. Here, an adhesives layer can dilute adhesives with a solvent as occasion demands, and can form them by applying and heating, drying to the upper-limit side of the pellicle frame 1, and stiffening it. In this case, as the method of application of adhesives, brush coating, a spray, the method by the automatic dispenser, etc. are mentioned.
[0014]
[Example] Next, an example is given and this invention is further explained to a detail. In addition, this invention is not limited to the following examples.
[0015] (Example 1) First, the frame made from an aluminium alloy with a ****** 100mmx100mmx6mm and a frame thickness of 2mm was prepared as a pellicle frame. After carrying out surface washing of this object, surface treatment was carried out for 10 minutes with sandblasting equipment with a discharge pressure of 1.5kg using the glass bead with a particle size of 90 micrometers, and the front face was roughened. Subsequently, after processing this thing for 10 seconds and washing it in a NaOH processing bath, it anodized and black-dyed, and sealing was carried out and the black oxide film was

formed in the front face. When the front face of the finished frame was measured with the surface roughness meter surfboard coder (made in the Kosaka lab, tradename), they were Ra0.45micrometer, Rt4.5micrometer, and RMS0.45micrometer. Pure water and the ultrasonic cleaner were used together and this aluminum frame was washed. Subsequently, spray coating equipment was used for this frame, and 10 micrometers of silicone system binders were coated. Subsequently, Teflon AF 1600 (the U.S. Du Pont make, tradename) was dissolved in fluorine system solvent FURORINATO FC-75 (the U.S. three em company make, tradename), and the solution of 8% of concentration was prepared. Next, the spin coater was used for the silicon machine plate surface with a diameter [of 200mm], and a thickness of 600 micrometers which carried out mirror polishing, and the transparent membrane whose membranous thickness is 0.8 micrometers was made to form with this solution. Next, on this film, epoxy system adhesives Araldite rapid (the Showa High Polymer Co., Ltd. make, tradename) was used, the frame with a 200mm x200mmx5mm width of face [of outside **] and a thickness of 5mm was pasted up, and it exfoliated underwater. Next, the frame made from an aluminium alloy which is the above, and was made and prepared was pasted up on the film front face of Teflon AF 1600 which formed membranes using epoxy system adhesives Araldite rapid (this forward). Two frames were fixed so that the adhesion side of a pellicle frame might be turned upward, it might attach in the fixture for fixation and a position might not shift relatively. Subsequently, the frame by the side of outside the limit pellicle] was pulled up, it fixed, and the tension of 0.5 g/cm was given to the film section by the side of outside the limit pellicle]. Moreover, 0.25mm in the cutter made from stainless steel and thickness was independently attached in the SCARA robot as an instrument for film cutting. Cutting removal of the unnecessary film portion by the side of outside the limit pellicle] was carried out moving a cutter along with the periphery of the adhesives portion on the aforementioned pellicle frame, while the tube formula dispenser was used for this cutter and 10micro/m of FURORINATO FC75 (this forward) was dropped 1 times. Next, when inspected having removed the unnecessary film portion and illuminating the inside of the obtained pellicle with a halogen lamp, the object considered to be a foreign matter by the front face did not exist, and did not have the scattered reflection of the light on the front face of a frame, either. Then, the standard particle made from polystyrene of 1.0 micrometers of particle diameters was made to adhere to a within the limit side. It has checked having adhered easily, when inspected illuminating this with a halogen lamp similarly. Moreover, when the dust particle inspection on the pellicle film using laser dispersion dust-particle-inspection equipment was conducted, there was no incorrect detection by the scattered light from a frame.

[0016] (Example 1 of comparison) First, the frame made from an aluminium alloy with a ****** 100mmx100mmx6mm and a frame thickness of 2mm was prepared as a pellicle frame. After carrying out surface washing of this object, surface treatment was carried out for 10 minutes with sandblasting equipment with a discharge pressure of 1.5kg using the glass bead with a particle size of 90 micrometers, and the front face was roughened. Subsequently, after processing this thing for 10 seconds and washing it in a NaOH processing bath, it anodized and black-dyed, and sealing was carried out and the black oxide film was formed in the front face. When the front face of the finished frame was measured with the surface roughness meter surfboard coder (this forward), they were Ra0.9micrometer, Rt9.1micrometer, and RMS1.2micrometer. Pure water and the ultrasonic cleaner were used together and this aluminum frame was washed. Subsequently, spray coating equipment was used for this frame, and 10 micrometers of silicone system binders were coated. Subsequently, Teflon AF 1600 (this forward) was dissolved in fluorine system solvent FURORINATO FC-75 (this forward), and the solution of 8% of concentration was prepared. Next, the spin coater was used for the silicon machine plate surface with a diameter [of 200mm], and a thickness of 600 micrometers which carried out mirror polishing, and the transparent membrane whose membranous thickness is 0.8 micrometers was made to form with this solution. Next, on this film, epoxy system adhesives Araldite rapid (this forward) was used, the frame with a 200mm x200mmx5mm width of face [of outside **] and a thickness of 5mm was pasted up, and it exfoliated underwater. Next, the frame made from an aluminium alloy which is the above, and was made and prepared was pasted up on the film front face of Teflon AF 1600 which formed membranes using epoxy system adhesives Araldite rapid (this forward). Two frames were fixed so that the adhesion side of a pellicle frame might be turned upward, it might attach in the fixture for fixation and a position might not shift relatively. Subsequently, the frame by the side of outside the limit pellicle] was pulled up, it fixed, and the tension of 0.5 g/cm was given to the film section by the side of outside the limit pellicle]. Moreover, 0.25mm in the cutter made from stainless steel and thickness was independently attached in the SCARA robot as an instrument for film cutting. Cutting removal of the unnecessary film portion by the side of outside the limit pellicle] was carried out moving a cutter along with the periphery of the adhesives portion on the aforementioned pellicle frame, while the tube formula dispenser was used for this cutter and 10micro/m of FURORINATO FC75 (this forward) was dropped 1 times. Next, when inspected having removed the unnecessary film portion and illuminating the inside of the obtained pellicle with a halogen lamp, many objects considered to be foreign matters by the front face existed. Then, although the pellicle inside was inspected using the stereoscopic microscope, the adhesion foreign matter was not accepted. Then, it made this clear that it is irregular reflection of the light on the front face of a frame. The standard particle made from polystyrene of 1.0 micrometers of particle diameters was made to adhere to a within the limit side here. When inspected illuminating this with a halogen lamp similarly, it has not distinguished from others and much scattered lights. Moreover, when the dust particle inspection on the pellicle film using laser dispersion dust-particle-inspection equipment was conducted, there was no incorrect detection by the scattered light from a frame.

[0017] (Example 2) First, the frame made from an aluminium alloy with a ****** 100mmx100mmx6mm and a frame thickness of 2mm was prepared as a pellicle frame. After carrying out surface washing of this object, surface treatment was carried out for 10 minutes with sandblasting equipment with a discharge pressure of 2.0kg using the glass bead with a particle

size of 90 micrometers, and the front face was roughened. Subsequently, after processing this thing for 10 seconds and washing it in a NaOH processing bath, it anodized and black-dyed, and sealing was carried out and the black oxide film was formed in the front face. When the front face of the finished frame was measured with the surface roughness meter surfboard coder (this forward), they were Ra0.5micrometer, Rt5.1micrometer, and RMS0.5micrometer. Pure water and the ultrasonic cleaner were used together and this aluminum frame was washed. Subsequently, spray coating equipment was used for this frame, and 10 micrometers of silicone system binders were coated. Subsequently, Teflon AF 1600 (this forward) was dissolved in fluorine system solvent FURORINATO FC-75 (this forward), and the solution of 8% of concentration was prepared. Next, the spin coater was used for the silicon machine plate surface with a diameter [of 200mm], and a thickness of 600 micrometers which carried out mirror polishing, and the transparent membrane whose membranous thickness is 0.8 micrometers was made to form with this solution. Next, on this film, epoxy system adhesives Araldite rapid (this forward) was used, the frame with a 200mm x200mmx5mm width of face [of outside **] and a thickness of 5mm was pasted up, and it exfoliated underwater. Next, the frame made from an aluminium alloy which is the above, and was made and prepared was pasted up on the film front face of Teflon AF 1600 which formed membranes using epoxy system adhesives Araldite rapid (this forward). Two frames were fixed so that the adhesion side of a pellicle frame might be turned upward, it might attach in the fixture for fixation and a position might not shift relatively. Subsequently, the frame by the side of outside the limit pellicle] was pulled up, it fixed, and the tension of 0.5 g/cm was given to the film section by the side of outside the limit pellicle]. Moreover, 0.25mm in the cutter made from stainless steel and thickness was independently attached in the SCARA robot as an instrument for film cutting. Cutting removal of the unnecessary film portion by the side of outside the limit pellicle] was carried out moving a cutter along with the periphery of the adhesives portion on the aforementioned pellicle frame, while the tube formula dispenser was used for this cutter and 10micro/m of FURORINATO FC75 (this forward) was dropped 1 times. Next, when inspected having removed the unnecessary film portion and illuminating the inside of the obtained pellicle with a halogen lamp, the object considered to be a foreign matter by the front face did not exist, and did not have the scattered reflection of the light on the front face of a frame, either. Then, the standard particle made from polystyrene of 1.0 micrometers of particle diameters was made to adhere to a within the limit side. It has checked having adhered easily, when inspected illuminating this with a halogen lamp similarly. Moreover, when the dust particle inspection on the pellicle film using laser dispersion dust-particle-inspection equipment was conducted, there was no incorrect detection by the scattered light from a frame.

[0018] (Example 2 of comparison) First, the frame made from an aluminium alloy with a ****** 100mmx100mmx6mm and a frame thickness of 2mm was prepared as a pellicle frame. After carrying out surface washing of this object, surface treatment was carried out for 10 minutes with sandblasting equipment with a discharge pressure of 1.5kg using the glass bead with a particle size of 40 micrometers, and the front face was roughened. Subsequently, after processing this thing for 10 seconds and washing it in a NaOH processing bath, it anodized and black-dyed, and sealing was carried out and the black oxide film was formed in the front face. When the front face of the finished frame was measured with the surface roughness meter surfboard coder (this forward), they were Ra0.2micrometer, Rt3.0micrometer, and RMS0.2micrometer. Pure water and the ultrasonic cleaner were used together and this aluminum frame was washed. Subsequently, spray coating equipment was used for this frame, and 10 micrometers of silicone system binders were coated. Subsequently, Teflon AF 1600 (this forward) was dissolved in fluorine system solvent FURORINATO FC-75 (this forward), and the solution of 8% of concentration was prepared. Next, the spin coater was used for the silicon machine plate surface with a diameter [of 200mm], and a thickness of 600 micrometers which carried out mirror polishing, and the transparent membrane whose membranous thickness is 0.8 micrometers was made to form with this solution. Next, on this film, epoxy system adhesives Araldite rapid (this forward) was used, the frame with a 200mm x200mmx5mm width of face [of outside **] and a thickness of 5mm was pasted up, and it exfoliated underwater. Next, the frame made from an aluminium alloy which is the above, and was made and prepared was pasted up on the film front face of Teflon AF 1600 which formed membranes using epoxy system adhesives Araldite rapid (this forward). Two frames were fixed so that the adhesion side of a pellicle frame might be turned upward, it might attach in the fixture for fixation and a position might not shift relatively. Subsequently, the frame by the side of outside the limit pellicle] was pulled up, it fixed, and the tension of 0.5 g/cm was given to the film section by the side of outside the limit pellicle]. Moreover, 0.25mm in the cutter made from stainless steel and thickness was independently attached in the SCARA robot as an instrument for film cutting. Cutting removal of the unnecessary film portion by the side of outside the limit pellicle] was carried out moving a cutter along with the periphery of the adhesives portion on the aforementioned pellicle frame, while the tube formula dispenser was used for this cutter and 10micro/m of FURORINATO FC75 (this forward) was dropped 1 times. Next, when inspected having removed the unnecessary film portion and illuminating the inside of the obtained pellicle with a halogen lamp, what is considered to be a foreign matter by the front face did not exist. Then, the standard particle with a particle size of 1.0 micrometers made from polystyrene was made to adhere to a within the limit side. It was easily detectable when inspected illuminating this with a halogen lamp similarly. Moreover, when the dust particle inspection on the pellicle film using laser dispersion dust-particle-inspection equipment was conducted, the incorrect detection by the scattered light from a frame appeared on the film near the frame.

[0019]

[Effect of the Invention] Since the pellicle of this invention can detect the foreign matter in the inside side of a pellicle frame certainly and easily, it can prevent the fall of the yield.

[Translation done.]